

SYNTHESIS, CHARACTERIZATION AND RHEOLOGICAL PROPERTIES OF GUARAN GRAFTED POLYACRYLAMIDE (G-G-PAM) COPOLYMER

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ABSTRACT: Guarán was transformed into grafted polymer using vinyl monomer. The vinyl monomer used for the graft was acrylamide. The grafting was initiated through the formation of free radical centers on the polymer backbone by oxidation of guarán with cerium (IV) in nitric acid medium. The degree of grafting was varied by using varying amount of acrylamide vinyl monomer. The rheological properties of the guarán grafted polyacrylamide copolymer have been studied by varying the degree of grafting, time, concentration, temperature, spindle number and shear rate. Thermal Characteristics of the guarán-grafted polyacrylamide was studied using thermo gravimetric analysis under nitrogen atmosphere. The prepared copolymer was characterized by FTIR.

Key words: Guarán, grafting; Vinyl monomer; Hydration time; Shear rate; Rheological properties.

INTRODUCTION

Polysaccharides are recently considered as the subjects for extensive worldwide academic and industrial research. In spite of potential applications of polysaccharides, it is necessary to establish efficient appropriate modifications to explore fully their high potential. A variety of chemical modifications are employed to modify these carbohydrate polymers. The present article provides a comprehensive technique on one of the most promising approaches to modify guarán, i.e., graft copolymerization, with an emphasis on the synthetic aspects.

The polymer grafts of varying degree of hydrophilicity and hydrophobicity can be incorporated into the strongly hydrophilic polysaccharide matrix. A wide range of vinyl monomers with varying degree of hydrophobicity may be grafted on to substrates such as starch (C.E. Brockway and P.A. Seaberg, 1967; Jianping, et. al., 1996), cellulose (K.C. Gupta and S. Sahoo, 2001), silk (Chen, et. Al., 2003), wool (Nayak, et. al., 1980; Giri, et. al., 1989), rubber (Lena, et al., 1985) and other polymers. Most of the vinyl grafting studies have been carried out on the carbohydrate; starch (Hamshary, et al., 2006; Song, et. al., 2007 and cellulose [C. Jett and J. Arthur, 1976].

The steady of shear and transient properties of starch in dimethylsulphoxide was investigated by (Kapoor and M. Bhattacharya, 2001). The rheological properties of xyloglucans (XG) from the extracellular medium of suspension cultured *Nicotiana plumbaginifolia* cells, apple pomace and tamarind seeds, with different structural features and molecular weights, have been studied by (Bacis, et. al., 1998).

The synthesis and rheological characterization of graft copolymer of Butyl and hydroxymethyl methacrylate on starches was investigated by (Gurrachaga, et. al., 2008). The studies of synthesis and thermal degradation of starch graft copolymer was carried out by (M. Zhang and Zi-heng Hu, 2002). Mechanical, thermal and rheological properties of methyl–methacrylate, styrene and copolymer were reported by (Zhue, et. al., 2009). Preparation and flocculation properties of cationic starch cross linking copolymer have been investigated by (You, et. al., 2009).

Synthesis of graft copolymer of cellulose with 4-acrylo morpholine and determination of some sorption properties was reported by (Temuz, et. al., 2007).

Srivastava and Behari studies of synthesis and characterization of Guar-g-N-Vinyl-2-pyrrolidone and investigation of metal ion sorption and swelling behavior (A. Srivastava and K. Behari, 2006).

The graft copolymer of guaran were considered to be of special interest, because of the unique structure of guaran matrix, which consists of a long straight chain of mannose residue with a sequence of galactose residue anchored to alternate mannose unit. Thus guaran offers a very regular matrix for synthesis of graft copolymer, incorporating desired physical and chemical properties. The viscosity, hydrophilic and hydrophobic nature of the graft, frequency of the grafting and the chain length of graft are of great significance in mineral processing (Karmakar et. al., 2002) and petroleum industry (Ibrahim, et. al., 2006). The morpholine guaran derivative (A. V. Singh and K.L. Menaria, 2001) has been employed for beneficiation of zinc sulphide ore from Rajpura Dariba Mines, Dariba, Udaipur, India.

Guaran is a polysaccharide-galactomannan obtained from the seeds of leguminous arid plant *Cymopsis tetragonolobus* Guaran and its derivatives have been extensively used for a number of applications, particularly oil well drilling, mining, paper, textile, food, cosmetic, pharmaceuticals, agriculture and number of other industries (B. L. Bansal and K. Kappor, 1984).

In the present paper, we are reporting our work on grafting of the polysaccharide guaran with polyacrylamide. The new Guaran Grafted Polyacrylamide was synthesized by the new technique of an oxidant–reductant system. In this technique free redial initiates the polymerization of Vinyl monomer. This technique preferred over thermal polymerization because they work at low temperature, good field of polymer is obtained, side reaction which occur higher temperature are negligible.

MATERIALS AND METHODS

Chemicals

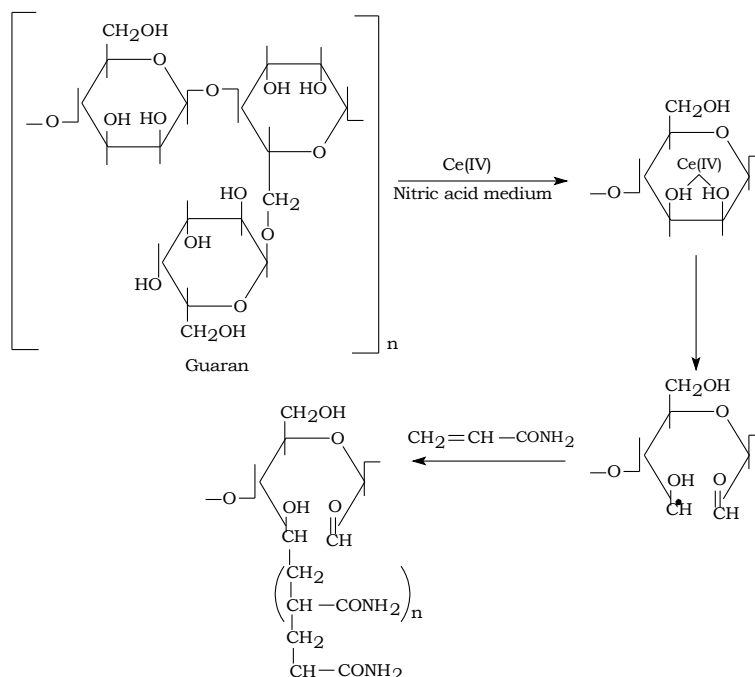
Analytical grade chemicals supplied by (Loba Chemic, Mumbai) were used in all experiments. Guaran powder was supplied by (Ases Chemical Works, Jodhpur, India). All other compounds used in the synthesis were of commercial high purity grade, and used without further purification

Preparation of Guaran Grafted Polyacrylamide (G-g-PAM)

Guaran solution (0.5%) was prepared by dispersing 5.0 g guaran in 1 liter distilled water in nitrogen atmosphere with constant stirring to avoid lump formation. Ceric ammonium nitrate reagent, 7ml (0.1M in 1M nitric acid) was added with constant stirring at 30°C. The stirring was continued for 30 minutes and 7.1g (0.1mole) acrylamide was added to the reaction mixture. The reaction mixture was stirred for four hour at 30°C. The product was recovered by precipitation with equal volume of ethanol and filtered under suction. The products was washed with aqueous ethanol (70, 80 and 90%) and finally with pure ethanol and dried under vacuum. An appreciable amount of guaran was recovered from aqueous filtrate. The grafted product was a light brown and fluffy powder. The mechanism for the synthesis of guaran-g-PAM copolymer is shown in reaction scheme-1. Guaran-g-PAM copolymer was analyzed for their nitrogen content by Kjeldal method. The nitrogen contents of 10.04% and 20.36% of guaran-g-PAM copolymer are found to be 1.94% and 3.64% respectively. The reaction scheme for synthesis of guaran-g-PAM is shown in Reaction scheme 1.

Characterization of Polyacrylamide Grafted Copolymer by IR Spectroscopy

Perkin Elmer IR 983 spectrophotometer was employed to run the spectra using KBr pellet. In IR spectra the broad band in the region $3600-3100\text{ cm}^{-1}$ may be assigned to primary hydroxyl group (C. N. R. Rao, 1963). The range of $2960-2830\text{ cm}^{-1}$ can be probably be assigned to various stretching frequencies of $-\text{CH}$ and $-\text{CH}_2$ groups. Another strong and sharp peak with a maximum of 1650 cm^{-1} may be due to $\text{C}=\text{O}$ stretching vibrations. The symmetric and asymmetric stretching mode of N-H vibrates at 3180 cm^{-1} and 3350 cm^{-1} respectively.



REACTION SCHEME I : GRAFTING OF ACRYLAMIDE ON GUARAN

The C-N stretching vibrates at 1400 cm^{-1} . The symmetric and asymmetric stretching modes of CH_2 group vibrate at 2926 cm^{-1} and 2853 cm^{-1} respectively. The N-H bending vibrates at 1665 cm^{-1} where as N-H wagging vibrates at the ranges of $800-666\text{ cm}^{-1}$.

The various bending vibrations of $-\text{CH}_2$ groups occur at 720 cm^{-1} , 1150 cm^{-1} , 1350 cm^{-1} and 1465 cm^{-1} . The IR spectra of guarane grafted polyacrylamide copolymer is given in figure.1.

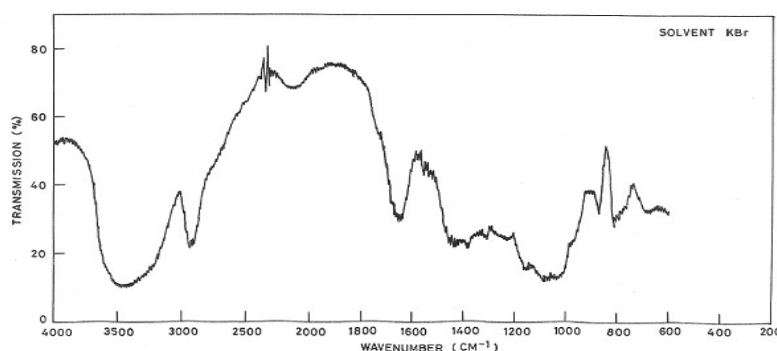


Figure.1. I.R. Spectra of Guarane Grafted Polyacrylamide Copolymer

Thermogravimetric Analysis:

For this purpose 951 thermogravimetric analyzer thermobalance was employed. The polymer sample was powdered to the same average mesh size and dried carefully in vacuum desiccator.

The boat was packed uniformly for analysis. For the dynamic measurement, the system was heated at a constant heating rate of 20°C per minute under static air atmosphere till the complete decomposition. The obtained TGA curve is shown in Fig.2. The polyacrylamide guaran copolymer is found to stable up to 362°C and then the degradation was found to be rapid.

Viscosity Measurements:

Viscosity of G-g-PAM was measured and the effects of different parameters, viz., concentration, temperature, shear rate and spindle size were studied. Measurements were made with Brookfield Synchro-Lectric Viscometer, RVT model, serial no.70156. For all viscosity measurements, a 1.0% aqueous solution of G-g-PAM was prepared by dissolving 1.0g of G-g-PAM in 99ml distilled water with vigorous stirring in order to avoid lump formation.

RESULTS AND DISCUSSION

The hydrophilic and hydrophobic character of the G-g-PAM was found to depend upon the nature of graft, percentage of grafting, and size of graft. It was observed that with the increase in the percentage of hydrophobic graft on the hydrophilic matrix, desired hydrophilic or hydrophobic character can be achieved. Rheological properties characterize the behavior of polymeric systems in deformation and flow of matter. Rheology includes the study of deformation forces as a function of hydration time, temperature, shear rate and certain other parameters. In the Newtonian systems the shearing stress is directly proportional to the rate of shear and viscosity is constant i.e. independent of shear rate. In non Newtonian system viscosity is not constant but is dependent on the shear rate. The results of variation in viscosities of G-g-PAM as a function of different parameters are represented in Figure. 3-6.

Effect of Hydration Time

It was observed that the rate of hydration of G-g-PAM studied was considerably lower than the parent polysaccharide. It is known that the parent ungrafted guaran requires about two hours attaining the maximum viscosity. However, in case of grafted products the attaining of the peak viscosity is delayed to the extent of twenty-four hours and thereafter it remains constant as shown in Fig.3, which depends upon percentage and nature of the grafts and the ultimate viscosity was also lower than parent guaran. On drying the graft copolymer, due to flexibility of the polymer chains, the grafts tend to aggregate and in hydration process these aggregates should be loosen by expanding the polymer structure. It was also observed that with increase in the percentage of vinyl graft the viscosity decreased as shown in Figure.4, which is attributed to the blocking of hydroxyl group in the parent polysaccharide chain by grafted –polymer chain .

Effect of Concentration

An exponential increase in viscosity with increase in concentration was observed as shown in Figure. 3 and 4. This behavior is similar to that of the parent polysaccharide. These results are reported in Tables 1, 2 and graphically represented in figures 3, 4.

Table-1 : Variation of Viscosity with Hydration Time of Guaran Grafted Polyacrylamide (D.G.10.04%) In Aqueous Solution of Different Concentration.

Parameters
Shear rate -20 rpm Spindle No. 3 Temperature – 25⁰C

Log t [minute]	Solution of concentration		
	[0.5%]	[1.0%]	[1.5%]
Hydration Time	Viscosity of Guaran-g-PAM in aqueous solution of concentration		
	[0.5%]	[1.0%]	[1.5%]
1.17	12	25	50
1.47	12	30	56
1.77	12	38	65
2.07	15	47	75
2.25	15	56	83
2.38	15	68	92
2.66	16	80	102
2.98	18	94	112
3.15	20	100	120
3.45	20	100	120
3.63	20	100	120

Table 2 : Variation of Viscosity with Hydration Time of Guaran Grafted Polyacrylamide (D.G. 20.36%) In Aqueous Solution of Different Concentration.

Parameters
Shear rate -20 rpm Spindle No. 3 Temperature – 25⁰C

Hydration time Log t [minute]	Viscosity of Guaran-g-PAM in aqueous solution of concentration		
	[0.5%]	[1.0%]	[1.5%]
1.17	25	325	450
1.47	25	520	650
1.77	25	650	900
2.07	25	760	1150
2.25	30	870	1375
2.66	30	998	1640
3.15	37	1086	1950
2.98	54	1207	2278
3.15	60	1300	2500
3.45	60	1300	2500
3.63	60	1300	2500

Table 3 : Effect of Shear Rate on Viscosity of Guaran-g-Polyacrylamide.

Parameters
Shear rate -20 rpm Spindle No. 3 Temperature – 25⁰C

Shear rate (rpm)	Viscosity (cps) of Guaran-g-PAM with different degree of grafting	
	[10.04%]	[20.36%]
10	50	800
20	100	1300
50	250	2200
100	575	3800

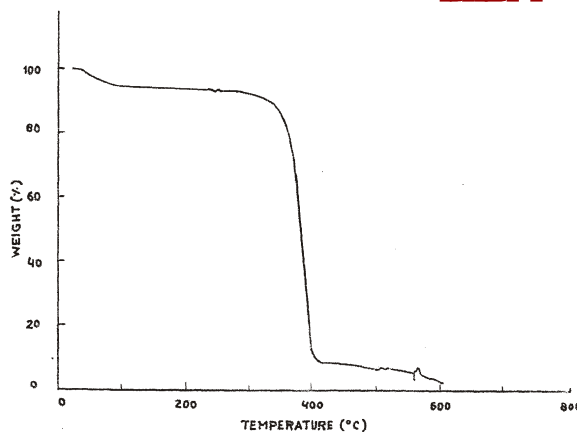


Figure. 2 TGA Curve of Guaran Grafted PAM Copolymer

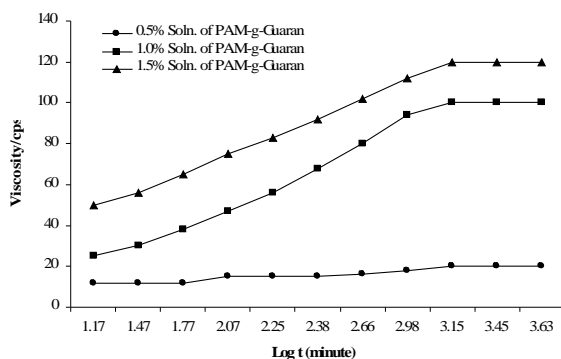


Figure.3. Variation of Viscosity with Hydration Time of G-g-PAM (D.G.10.04)

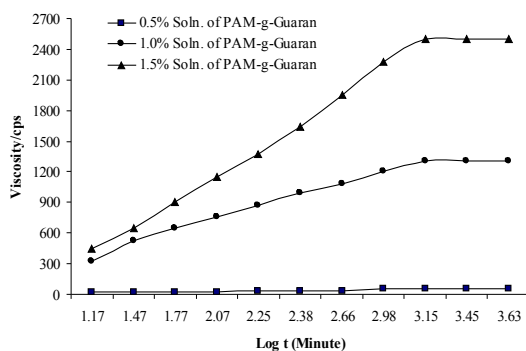


Figure.4. Variation of Viscosity with Hydration Time of G-g-PAM (D.G 20.36%)

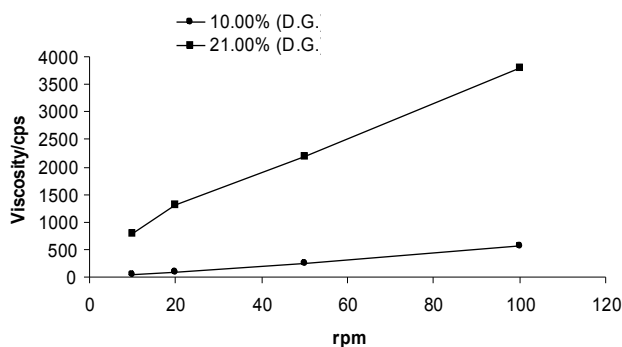


Figure.5. Variation of Viscosity of G-g-PAM with Shear Rate

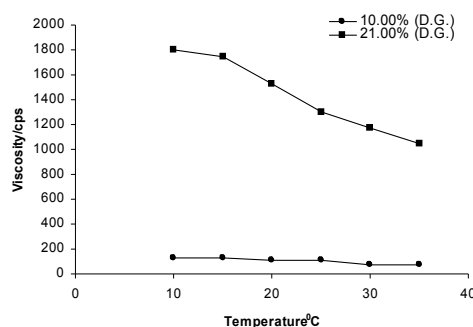


Figure. 6 Variation of Viscosity of G-g-PAM with Temperature ($^{\circ}$ C)

Effect of Shear Rate

Prabhanjan and Ali (H. Prabhanjan and S. Z. Ali, 1995) studied the shear dependence and pseudoplastic flow behavior characteristics of carboxymethyl and hydroxypropyl derivatives of tamarind kernel powder. The chemical modification decreased the shear dependence of the solution viscosity as the degree of substitution increased.

In the case of G-g-PAM, it was observed that with increase in shear rate, the viscosity also increases as shown in Fig. 5 (Table3), which suggests the flow to be non-Newtonian in character. Generally, the water dispersions of hydrocolloids show non-Newtonian flow behavior and undergo shear-thinning. Surprisingly the G-g-PAM showed shear-thickening. There is however no increase in volume, i.e., dilatancy effect, a phenomenon associated with pastes. Hence the shear-thickening appears to be due to particle aggregation caused by the interaction between the long chain acrylamide grafting on the polysaccharide backbone. As the shear rate increases, the transition shifts from low to high concentration solution due to long chain acrylamide grafting. The interaction of long chain grafting acrylamide is also strengthened from I.R. spectra as shown in Figure.1

Effect of Temperature:

The viscosity of G-g-PAM was found to decrease with the increase in temperature as shown in Fig. 6. This behavior is similar to that of parent polysaccharide.

It was also observed that with the increase in the percentage of acrylamide grafting, the viscosity further decreases due to blocking of hydroxyl group in the parent polysaccharide chain by acrylamide grafting. . The results are reported in Tables 4.

Table 4 Effect of Viscosity of Guaran-G-Polyacrylamide with Temperature.

Parameters		
Shear rate - 20 rpm	Spindle No. 3	Concentration of solution – 1.0%
Temperature 0°C	Viscosity (cps) of Guaran-g-PAM with different degree of grafting	
	[10.04 %]	[20.36%]
10	125	1800
15	125	1750
20	112	1525
25	110	1300
30	75	1175
35	75	1050

Effect of Different Spindles:

A little change in viscosity was observed when measurements were made with different spindles. The constancy of viscosity on changing the spindle establishes the validity and reliability of the measurements.

Conclusions

The Polyacrylamide graft copolymer of guaran was considered to be of special interest because of the unique structure of the guaran matrix. The guaran offers a very regular linear matrix suitable for incorporating the desired physical and chemical properties through appropriate grafting and crosslinkage. The viscosity, hydrophilic-hydrophobic nature of the graft, degree of grafting and chain length of the graft is of great significance in mineral processing and petroleum industries (A. Asatekin and A. M. Mayes, 2009).

Acknowledgments

The Authors are thankful to University Grants Commission, New Delhi, for providing the financial support during this investigation.

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